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54 Electrically conductive plastic complex material.

57 An electrically conductive plastic complex material comprises a mixture of the synthetic base resin material, an electrically conductive carbon black and at least one inorganic filler selected from graphite, calcium carbonate, talcum, alumina and titania. Doped graphite or active carbon may also be included.

The material is especially suitable for use as an electrode for metal-halogen batteries because of its resistance to diffusion of halogen and to degradation, while its volume resistivity is not affected by variations in temperature.

## Electrically Conductive Plastic Complex Material

This invention relates to an electrically conducting plastic complex material endowed with higher than a certain value of electrical conductivity without inclusion of metallic contents and more particularly to such electrically conductive plastic complex material suitably used in conjunction with electrical, electronic or electrochemical devices such as metal-halogen batteries.

Recently, the use of a electrically conductive plastic complex material has become widespread not only in electrical devices for domestic use but as computer components or electrodes for recently developed metal-halogen batteries.

These electrically conductive plastic complex materials are used as so-called molded pieces or synthetic resin paint and are usually manufactured by dispersing fine powders of Ag, Cu, Al or the like metals or fine carbon particles into the synthetic resin.

Since the electrically conductive plastic complex materials are prepared by simply dispersing electrically conductive substances into the non-conductive plastic material, their electrical conductivity may be fluctuated widely by non-homogeneous dispersion of the conducting particles. In addition, it has not been possible to increase the electrical conductivity beyond a certain limit although some electrically conductive complex with contents of the dispersed metallic

powders exhibit an electrical conductivity of the order of  $10^4$  to  $10^5 \text{ ohm}^{-1} \text{ cm}^{-1}$ . The result is unavoidable limitation on the application of the electrically conductive plastic complex material.

Recently, it has been proposed to make use of certain dopants that may affect polyacetylene, polypyrrole or polyparaphenylene sulfide so as to make them electrical conductivity. However, the resulting material tends to be unstable in physical properties and the apparatus for producing it is also complicated in structure.

In general, the insulating materials such as plastics, semi-conductors such as Ge, Si, carbon black or graphite or conductors such as metal have intrinsic volume resistivity proper to them.

The volume resistivity for the insulating material is higher than  $10^8 \text{ Ohm-cm}$ , while that for semi-conductors is  $10^{-3}$  to  $10^8 \text{ ohm-cm}$  and that for conductors is less than  $10^{-3} \text{ ohm cm}$ .

The volume resistivity of these electrical materials change in accordance with variation of temperature.

Thus, the volume resistivity of the insulating material generally decrease with rise in temperature, while that of the semiconductors and that of conductors increase with rise in temperature. An electrically conductive complex material obtained by mixing carbon black into the base polymer and kneading them together is lightweight and low in cost while also exhibiting good workability. Hence it is employed in a variety of electrical devices.

However, the volume resistivity of this material also tends to increase with rise in temperature.

The result is that the electrical or electronic devices which make use of the carbon black mixed into the base polymer material undergo changes in their properties in accordance with variation of temperature and hence are not capable of keeping constant properties.

The plastic complex materials used in electrolytes (electrolytic solutions) tend to be affected by materials produced upon electrolysis and thus undergo certain chemical degradation. This tendency is most outstanding especially in cases wherein the substances produced upon electrolysis are-halogen group elements such as chlorine or bromine.

The term electrolytic solution as used in the present specification is intended to mean the electrolyte used in storage battery as well as electrolyte for dry battery or electroplating accompanying electrochemical reactions. It is an aqueous solution of compounds of a halogen group element selected from the group consisting of F, Cl, Br and I with at least one alkali or alkali earth metals such as Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs or Ba in addition to metals such as Zn, Cu, Ni, Co, Fe, Mn, Cr, Sn, Pb, Pt, Hg, Cd, Ag or Pd.

The inventive materials may also be used with electrolytes from which strong acid groups, substances that extract hydrogen from hydrocarbons in the plastic complex material, strongly reductive agents, or compounds such as strong alkali that may act as hydrolytic agent, such as  $O$ ,  $O_2$ ,  $O_3$ ,  $S$ ,  $SO_2$ ,  $SO_3$ ,  $SO_4$ ,  $ClO_3$ ,  $CrO_3$ ,  $OH$ ,  $O_2H$  or  $MnO_3$  are

produced upon decomposition of the electrolytes.

In general, when dipped in these electrolytes or exposed in chlorine or bromine liquids for accelerated degradative tests, the plastic complex material may become swollen in a short period and broken up into pieces which is extremely undesirable from the standpoint of dimensional stability and mechanical strength.

This means that the plastic complex material is subject to molecular cleavage or disruption when acted on by electrolytic products such as chlorine or bromine thus leading finally to failure of the material.

In recent years, the necessity for more effective energy utilization has led to development of a novel type battery making use of metal-halogen as active material. An example of such metal-halogen battery is shown in Fig. 1 which shows in exploded perspective the laminated or stacked structure of the metal-halogen secondary battery through which the electrolyte is circulated.

In Fig. 1, electrodes 1 of the bipolar type and separators 2 are stacked as shown and clamped on both sides by aluminium clamping end plates 11. The stack of these electrodes and separators are united together by bolts 12 and nuts 13. The electrolyte is supplied from a manifold 14 through a channel 15 and a microchannel 19 to the electrode surface and kept in circulation by means not shown. In the drawing, the numeral 16 designates a plastic clamping end plate, the numeral 17 an electrode end plate and the numeral 18 a terminal comprised of a wire net.

The aforementioned metal-halogen battery makes use of:

monovalent alkali metals such as Li, Na or K or divalent metals such as Zn, Cd, Ni, Co or Fe as metals, Cl, Br or I as halogen and aqueous or nonaqueous solutions as electrolyte. So far, the electrodes comprising a mixture of a synthetic resin material and electrically conductive substances such as metal powders or carbon powders have been used in connection with the aforementioned metal-halogen batteries because these electrodes can be fabricated at lower costs into desired shape because of improved formability of the aforementioned mixture and are excellent in halogen durability. However, these electrodes are defective in that halogen diffuse on long period usage from one towards the other side of the electrode, consequently self-discharge occurs and thus loses the function of storage batteries. Thus, when the halogen penetrates through the electrode, problems are caused such that i) the outer battery casing is damaged by corrosive action; ii) the energy efficiency of the battery is reduced in proportion to the penetrated halogen; iii) above all, the bipolar type battery is subject to self-discharge due to halogen penetration; and iv) the electrode may be degraded by halogen diffusion in the electrolyte.

In sum, the conventional electrically conductive plastic complex material is defective in that its volume resistivity is high and changes in accordance with variation of temperature; the constituting molecules of the plastic material are subject to disruption or cleavage in the electrolyte thus introducing to failure of the material; and, when the material is used as electrode of the metal-

halogen secondary battery and used in an electrolyte, halogen penetration may be caused from one side to the other side of electrode thus occurrence of self-discharge and the resulting battery failure.

It is therefore a primary object of the present invention to provide an electrically conductive plastic complex material which is free from the defects of the conventional material and exhibits the high electrical conductivity and mechanical strength with the use of the commercial materials and in which volume resistivity is not affected by variation of temperature.

It is a further object of the present invention to provide such material that has a long life time and is not degraded when used in electrolytes with lapse of time.

It is a further object of the present invention to provide an electrode for a metal-halogen battery in which halogen as active material penetrates very slightly through the electrode.

The present invention relates to an electrically conductive plastic complex material comprizing a synthetic resin base material added with electrically conductive carbon black and inorganic filler, and characterized in that the inorganic filler is at least one selected from the group consisting of graphite, calcium carbonate, talcum, alumina, silica and titania.

According to the present invention, graphite used as inorganic filler is graphite treated by a dopant and active carbon is added to and mixed with graphite, the resulting mixture being formed to an electrically conductive plastic complex material product. The resulting formed article may be used as electrode for metal halogen battery or as components of electrical and electronic devices.

Fig. 1 is an exploded perspective view showing the stacked structure of the metal-halogen secondary battery with circulation of the electrolyte therethrough.

Fig. 2 is a graphic chart showing temperature characteristics of the volume resistivity for the Examples of the present invention and comparative Examples.

Fig. 3 is a diagrammatic view showing a unit for measuring bromine penetration.

Fig. 4 is a graphic chart showing the bromine penetration with time lapse through the plastic electrodes as confirmed by the Examples.

Among base materials of the plastic complex material contemplated within the scope of the present invention are thermosetting resins such as phenol, urea, melamine, epoxy, or alkyd, thermoplastic resins such as polyolefin, polystyrene, PMMA, polyvinyl acetate, PVA, polyvinylidene chloride or nylon, synthetic resin paint containing these resins, silicon rubbers such as SBR, butadiene rubber,



polyisoprene rubber, EP rubber, NBR or polyurethane rubber, and a variety of synthetic fibers.

In order to attain the second and third objects of the present invention, it is preferred to use one or more of the polyolefins such as high density polyethylene, normal chains type low density polyethylene, polypropylene or ethylene-propylene copolymer. Halogen durability of the resultant material may be improved by using the base synthetic resin material with density higher than  $0.94 \text{ g/cm}^3$  in polyethylene  $0.90 \text{ g/cm}^3$  in polypropylene and  $0.90 \text{ g/cm}^3$  in ethylene-propylene copolymer.

As electrically conductive carbon black, various products resulting from incomplete combustion or heat cracking of natural gas or liquid hydrocarbons may be used. However, the electrically conductive carbon blacks having the particle size in the range of 30 to 46nm, surface area in the range of 245 to  $1000 \text{ m}^2/\text{g}$ , volatile matter contents in the range of 1 to 1.5 weight percent, pH in the range of 7.0 to 9.5 and DBP oil absorption in the range of 160 to 340 ml/100g, are most preferred.

Although graphite can be used as it is, it may also be doped for further improving electrical conductivity of the conductive plastic complex material.

Among dopants to be used for this purpose are bromine, iodine, iodine chloride, iodine bromide, sulfuric acid, nitric acid and arsenic(V) fluoride.

Among active carbon added besides the aforementioned inorganic fillers are powdered or granulated active carbon such as pelletized, crushed, granulated powder or spherical

carbon that are activated with chemicals or steam.

In consideration of the shortcomings of the aforementioned conventional electrically conductive plastic complex materials, the present inventors conducted repeated researches into various compositions of the synthetic base resin material (A), electrically conductive carbon black (B) and a variety of inorganic fillers (C). These mixtures were kneaded in a mixer or roll kneader, and then formed by a conventional forming machine to a desired shape and the properties of these formed pieces were measured. The present invention has been completed on the basis of the information derived from these experiments, and resides in an electrically conductive plastic complex material comprising a synthetic base resin material (component A), electrically conductive carbon black (component B) and inorganic filler (component C) which is one or more ingredients selected from the group consisting of graphite, calcium carbonate, talcum, alumina and titania, said electrically conductive plastic complex material being formed and used in electrolytes, that is, as electrode made from complex material.

It has been shown from the Examples that, when the graphite or doped graphite is used as component C, the electrically conductive plastic complex material of the present invention is comprised of 30 to 80 wt. percent and preferably 30 to 70 wt. percent, and most preferably 45 to 65 wt. percent of the component A, 5 to 40 wt. percent and preferably 5 to 35 wt. percent and most preferably 5 to 35 wt. percent of the component B and 5 to 65 wt. percent and preferably 15 to 65 wt. percent and most preferably 15

to 50 wt. percent of the component C, related to the total of the components. With the component A lower in contents than those specified above, the resulting material is lowered in pliability and mechanical strength. With the component A higher in contents than those specified above, it is not possible to realize sufficient electrical conductivity.

The electrically conductive plastic complex material of the aforementioned composition can be manufactured by using the conventional forming apparatus and endowed with excellent formability and electrical conductivity without significantly lowering its mechanical strength.

It has also been shown from the Examples that, with talcum used as inorganic filler and olefinic thermoplastic resins such as polyethylene, polypropylene, or ethylene-propylene copolymer as component A, and with the contents of the electrically conductive carbon black (component B) and talcum (component C) respectively contain 5 to 50 wt. percent, the balance being the component A, the resulting electrically conductive plastic complex material is not affected with variation of temperature, as has also been confirmed in the Examples.

The electrically conductive carbon (component C) is contained in the range of 5 to 50 wt. percent because the electrically conductive plastic complex material is lowered in electrical conductivity for carbon contents less than 5 wt. percent and the material becomes difficult to formation for carbon contents higher than 50 wt. percent. On the other hand, talcum (component C) should be contained

in the range of 5 to 50 wt. percent in consideration that volume resistivity of the material may be affected with variation of temperature for talcum contents less than 5 percent and becomes difficult to formation for talcum contents higher than 50 percent.

The electrically conductive plastic complex material of the present invention is not affected substantially in volume resistivity so that the electric or electronic devices made from this material also exhibit stable performance in spite of occasional variation of temperature. The inventive material is not affected substantially in volume resistivity, and thus may not consider the temperature variation of devices.

The present inventors conducted a research into possible additives that will enable the ultimate plastic complex material exposed to electrolytes to be more durable and less susceptible to the electrolytes.

Thus a zinc bromide aqueous solution has been selected as electrolyte because it produces bromine (which is most aggressive) and also because it may be present as bromine aqueous solution when electrolyzed. A variety of polyolefins have been tested as to their durability to electrolytic products.

It is seen from the Examples described below that the electrically conductive plastic complex material comprising a mixture of the synthetic base resin material, electrically conductive carbon black and at least one of calcium carbonate, talcum, alumina, silica and titania as inorganic filler shows extremely divergent properties according as the polyolefin density lies above or below a critical value of  $0.94 \text{ g/cm}^3$

in polyethylene.

From this it has been confirmed that the durability of polyolefin to chemicals is closely related with the degree of cristallinity of the polyolefin employed and remains unaffected by the particular polymer type (such as block polymer or random polymer) and that the aforementioned critical effects may be derived solely by regulating the density of the synthetic base resin material.

Thus, the higher in the density of the polyolefin employed the better will be the durability of the resulting material to electrolytic products. However, as the polyolefin density is increased, the rate of increase in stability of the ultimate material is gradually lowered. On the other hand, the ultimate plastic complex material is lowered in formability with increase in density. Therefore it is practically desirable that polyolefin density be in the range of about  $0.94 \text{ g/cm}^3$  to  $0.98 \text{ g/cm}^3$  in polyethylene.

When the inorganic filler is to be added to the composition of the inventive material, it may be preferred that polyolefin, electrically conductive carbon black and the inorganic filler be in the ranges of 18 to 50, 1 to 25 and 25 to 75 wt. percents, respectively.

The present inventors conducted repeated researches into compositions of electrode materials capable of obviating the aforementioned deficiency accrued from use of the carbon-plastic electrodes in conjunction with metal-halogen batteries. It has emerged from these researches that the electrode formed by an electrically conductive plastic complex material comprized of a basic composition

(carbon-plastic composition) consisting of the synthetic base resin material, carbon black and graphite and highly adsorptive active carbon operative to inhibit diffusion into electrode of the active material (halogen) is effective to drastically reduce halogen diffusion while also reducing an electrical resistivity of electrode as compared with the conventional carbon-plastic electrode and markedly improving the energy efficiency of the storage battery.

The novel electrode composed of the electrically conductive plastic complex material may be obtained by using active carbon as an adsorptive agent showing good adsorptivity and low electrical resistivity, adding 1 to 30 wt. percent of the active carbon into a carbon-plastic composition comprising a base synthetic resin material or matrix such as high-density polyethylene, normal chain type low-density polyethylene, polypropylene or ethylene-propylene copolymer, or another polyolefin, carbon black and graphite, and forming the mixture to a desired-shaped product. The composition is heated in a pressure kneader with an initial temperature of  $180^{\circ}\text{C}$ , kneaded thoroughly, pre-heated at 150 to  $170^{\circ}\text{C}$  and formed to a desired-shaped electrode by using a heating press machine at a pressure of  $100\text{ kg/cm}^2$ . The amount of the diffused halogen was measured with a device shown in Fig. 3. Thus it has been shown that the electrode comprised of active carbon and the aforementioned basic composition has superior properties to those of the electrodes consisting of the conventional carbon plastics.

Referring to the measurement unit shown in Fig. 3, the numeral 21 designates a disk-shaped sample sheet having a

liquid contact surface 20mm diameter and 1mm thickness. The numeral 23 designates a vessel containing 25 ml of an electrolyte 27 containing no bromine (3 mol of  $\text{ZnBr}_2$  per liter of aqueous solution), and the numeral 24 a vessel containing 25 ml of an electrolyte 26 containing bromine (3 mol of  $\text{ZnBr}_2$  per liter and 3 mol of  $\text{Br}_2$  per liter of aqueous solution). The numeral 22 designates a packing, the numeral 25 a tightening bolt and the numeral 28 a cap adapted for preventing vaporization of the electrolyte.

In operation, the electrode sheet 21 is introduced into the vessel 23. The vessel 24 is tightened in a leakage free manner with the aid of the packing 22 and the tightening bolt 25. The electrolyte 26 containing bromine and the electrolyte 27 containing no bromine are introduced to the same level to eliminate the difference in liquid head. After lapse of a predetermined time, the amount of bromine ( $\text{Br}_2$ ) diffused from the electrolyte 26 into the electrolyte 27 is measured with the aid of iodometry.

As seen from the Examples No. 12 below, the inventive electrode made from electrically conductive plastic complex material comprized in turn of the carbon-plastic composition and active carbon shows a electrical resistivity equal to 0.1 to 0.11 ohm cm as electrode characteristics which represents about 60 percent of the resistivity for the conventional electrode comprized only of carbon-plastic material. The inventive electrode also showed a tensile strength equal to 370 to 375  $\text{kg/cm}^2$  which is higher about 25 percent than the value for the conventional electrode. When immersed for 500 hours in a 95%-bromine liquid at room

temperature, the inventive electrode showed a reduction only 3 to 4 percent of total strength and an increase only 3 to 6 percent of resistivity. The inventive electrode also showed markedly reduced bromine diffusion as compared with the conventional electrode as shown in Fig. 4 which shows the data obtained by using the aforementioned measurement unit. The inventive electrode may therefore be used advantageously as electrode made from the complex material..

In consideration of the electrical conductivity of the electrode and the mechanical strength and workability, 1 to 30 wt. percent of active carbon is included in the composition as adsorbant. The amount of the graphite may be adjusted correspondingly. Active carbon may be pulverulent or granular, and may be in the pelletized, crushed, granulated powder or spherical form, activated with steam or chemicals.

The inventive electrode formed by electrically conductive plastic complex material added with active carbon has the following advantages.

- (i) It is formed and composed of synthetic resin material, carbon black, graphite and active carbon and hence it is capable of suppressing diffusion of the halogen, such as bromine as active material. The result is the drastically improved energy efficiency of the storage battery.
- (ii) Diffusion of the halogen (such as bromine) through the electrode is reduced so that the electrode plate



is free from its aggressive action resulting in long life time of the electrode.

- (iii) The effect discussed in item (ii) may also be obtained with the end electrode plate and the outer battery casing.
- (iv) The inventive material may be manufactured at reduced costs and used advantageously not only with the metal-halogen battery such as bromine-zinc or chlorine-zinc battery but with other batteries making use of electrodes made from electrically conductive plastic complex material or electrodes designed use for with electrochemical reactions.

The present invention will be described further by referring to the Examples below.

In evaluation, referential dumbbell samples (thickness, about 1mm) were prepared in accordance with JIS Z 1703 and their tensile strength was measured with the use of a tensile tester. The relation between the tensile strength of the tested sample and that of the untested sample was expressed in terms of the tensile strength retention ratio (percent).

The test is the accelerated degradative test in which each sample was immersed in 94% - bromine solution for 1000 hours at room temperature.

The names and certain physical properties of the synthetic resin material (A), electrically conductive carbon black (B) and the inorganic filler (C) used in the Examples and Comparative Examples are shown in the following Table 1.

Table 1. Names and Properties of Components

	Commercial Name	Maker	Physical properties				Ex. No.	Comp. Ex. No.
			Density (g/cm <sup>3</sup> )	m.p. (°C)	Softening point (°C)	MFR (g/10 min)		
Synthetic resin material (A)	A <sub>1</sub>	5000 SF	Mitsui Sekiyu Kagaku K.K.	0.959	132		0.75	1-(1) 3-(2) 7-(3) 1-1, 4-3
	A <sub>2</sub>	FX0860	Showa Denko K.K.	0.953		129	0.8	1-(4) 3-(5) 7-(2) 1-2, 4-2
	A <sub>3</sub>	S6008	"	0.958		129	0.8	3-(1) 6-(4) 6-(5)
	A <sub>4</sub>	Stafron E908(F)	Nippon Sekiyu Kagaku K.K.	0.950	129		0.08	6-(1) 6-(6) 3-1
	A <sub>5</sub>	Stafron E703	"	0.961	129		0.3	6-(2)
	A <sub>6</sub>	Showrex S6006M	Showa Denko K.K.	0.957		128	0.5	6-(3) 6-(7)
	A <sub>7</sub>	Showrex S4002	"	0.935		119	0.2	3-2
	A <sub>8</sub>	M850	Chisso K.K.	0.963	132		5.3	8-(1) 8-(2) 8-(3) 5-1

Table 1. (Continued)

	Commercial Name	Maker	Physical properties				Ex. No.	Comp. Ex. No.
			Density (g/cm <sup>3</sup> )	m.p (°C)	Softening point (°C)	MFR (g/10 min)		
Synthetic resin material (A)	A <sub>9</sub> polypropyrene	MS 230 Tokuyama Soda K.K.	0.91	150		4	1-(2) 3-(3) 5 7-(4)	4-4
	A <sub>10</sub> ethyrene-propylen-copolymer	MS 660 "	0.9	150		15	1-(3)	
	A <sub>11</sub>	MS 640 "	0.9	150		6.5	3-(4)	
	A <sub>12</sub>	MS 624 "	0.9	150		2	7-(1)	4-1
	A <sub>13</sub> phenol denatured oil vanish	#120B Union Kasei K.K.	-	-		-	2 4	2
elec, cond. carbon black (B)			Absorption (ml/100g)	N <sub>2</sub> Surface Area (m <sup>2</sup> /g)				
	B <sub>1</sub> CONDUCTEX -975	Columbia Carbon K.K.	160	270			1-(1) 3-(4) 7-(3)	4-3
	B <sub>2</sub> Ketchen black EC	Lion Acso K.K.	350	950			1-(2) 1-(4) 2 3-(1) 3-(2) 3-(5) 4 5 6-(2) 6-(4) 6-(5) 8-(1) -(3)	3-2 5-1

Table 1. (Continued)

Elec. cond.	Commercial Name	Maker	Absorption (ml/100g)	N <sub>2</sub> Surface Area (m <sup>2</sup> /g)	Ex. No.	Comp. Ex. No.
Carbon black (B)	B <sub>3</sub>	CABOT	166	272	1-(3) 3-(3) 6-(3) 6-(7) 7-(2) 7-(4)	1-2 4-2 4-4
	B <sub>4</sub>	Nippon Columbia K.K.	175	245	6-(1) 6-(6) 7-(1)	3-1 4-1
Inorganic filler (C)	Graphite C <sub>1</sub>	Tokai Carbon K.K.	particle size -200 mesh		1-(1) 1-(2) 1-(3) 1-(4) 2, 5 8-(1) 8-(2) 8-(3)	1-1 2 5-1
	doped	"	bromine dopant liquid		3-(1)	
	gra-phite	"	iodine acetone solution		3-(2)	
	C <sub>1-3</sub>	"	3 mol iodine chloride/1 lit. methanol		3-(3)	
	C <sub>1-4</sub>	"	iodine bromide		3-(4)	
	C <sub>1-5</sub>	"	sulfuric acid		3-(5)	
	C <sub>1-6</sub>	"	nitric acid		4	
	C <sub>1-7</sub>	"	arsenic fluoride (V)		5	

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Table 1 (Continued)

	Commercial Name	Maker	Powder particle size	Analysis (wt. %)						Ex. No.
				SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Ig. loss	
Talcum	C <sub>2-1</sub>	Talcum K.K.	-300 mesh	61.7	31.1	0.8	0.9	0.2	5.3	7-(1) 7-(3)
	C <sub>2-2</sub>	"	-350 mesh	62.3	36.7	0.1	0.8	0.2	4.9	6-(3) 7-(2) 7-(4)
				specific gravity	mean particle size (μm)	particle size	Surface area (cm <sup>2</sup> /g)			
Crystallite	C <sub>3</sub>	K.K. Tatsumori		2.6	1.9	+200 mesh	+325 mesh	18000		6-(4)
Soda Alumina	C <sub>4</sub>	Showa Keikinzoku K.K.		3.99			10% 70%			6-(5) 6-(7)
TiO <sub>2</sub>	C <sub>5</sub>	Ishihara Sangyo K. K.		4.2	0.213					6-(6)

Inorganic filler (C)

## Example 1

The starting materials of the following composition were injected into a pressure kneader heated to 160°C and were kneaded for 15 minutes. The kneaded materials were formed by calender rolls to sheets 1mm thick and the electrical conductivity as well as tensile strength of the resulting samples were measured. The results are shown in the Table 3.

Test No.	1-(1)	1-(2)	1-(3)	1-(4)
synth. resin mat.	A <sub>1</sub> , 60%	A <sub>9</sub> , 65%	A <sub>10</sub> , 55%	A <sub>2</sub> , 50%
elec. cond. carb. black	B <sub>1</sub> , 10%	B <sub>2</sub> , 5%	B <sub>3</sub> , 15%	B <sub>2</sub> , 5%
inorgan. filler	C <sub>1</sub> , 30%	C <sub>1</sub> , 30%	C <sub>1</sub> , 30%	C <sub>1</sub> , 45%

## Example 2

Synthetic resin paint A<sub>13</sub> (55 wt. percent of the total) was introduced into a three-roll calender and conductive carbon black B<sub>2</sub> (10 wt. percent) with graphite C<sub>1</sub> (35 wt. percent) was gradually added thereto. The resulting mixture was kneaded to an electrically conductive paint and the properties of the resulting samples were measured. The results are shown in Table 3.

## Comparative Example 1

The materials of the composition shown below were kneaded as in Example 1. The properties of the resulting samples are shown in Table 3.

Test No.	1 - 1	1 - 2
synth. resin mat.	A <sub>1</sub> , 50%	A <sub>2</sub> , 50%
elec. cond. carbon black	-	B <sub>3</sub> , 10%
inorg. filler (graphite)	C <sub>1</sub> , 50%	-

### Comparative Example 2

The starting material consisting of 60 wt. percent of the synthetic resin material A<sub>13</sub> and 40 wt. percent of graphite C<sub>1</sub> were kneaded in the manner as described in Example 2 and the properties of the resulting samples were measured. The results are shown in Table 3.

### Example 3

A pressure kneader consisting of a ceramic mixer tank was set to 150°C and the starting materials consisting of polyolefine synthetic resin material (A), carbon black (B) and doped graphite (C) were kneaded under kneading conditions  $\alpha$ ,  $\beta$  and the kneaded materials were pressed by calender rolls into sheets each 1mm thick. The properties of the resulting sheets as measured are shown in Fig. 3.

Doped samples were obtained by immersing powdered graphite in a dopant for 20 hours. Excess dopant was removed by allowing the graphite to stand for 4 to 5 hours in a draft at room temperature after the graphite was removed from the liquid. The  $\alpha$  condition refers to kneading in which the components A and B are kneaded for 10 minutes, then the component C is added to the resulting kneaded product and

and the resulting product with additive C is kneaded for 2 minutes, and the  $\beta$  condition to kneading in which a mixture of the components A, B and C are kneaded together for 15 minutes. The dopants used are also shown in Table 2.

Table 2

Composition and Kneading Conditions  
(the numeral. is weight percent)

test No.		3 - (1)	3 - (2)	3 - (3)	3 - (4)	3 - (5)
Composition	synth. resin mat. (A)	A <sub>3</sub> , 10	A <sub>1</sub> , 50	A <sub>9</sub> , 50	A <sub>11</sub> , 50	A <sub>2</sub> , 60
	carbon black (B)	B <sub>2</sub> , 10	B <sub>2</sub> , 10	B <sub>3</sub> , 30	B <sub>1</sub> , 30	B <sub>2</sub> , 10
	doped graphite (C)	C <sub>1-1</sub> , 30	C <sub>1-2</sub> , 40	C <sub>1-3</sub> , 20	C <sub>1-4</sub> , 20	C <sub>1-5</sub> , 30
dopant		bromine liquid	iodine acetone solution	iodine chloride 3 mol in 1l methanol	iodine bromide (50°C)	sulfuric acid
knead. cond.		$\alpha$	$\beta$	$\alpha$	$\alpha$	$\beta$

## Example 4

Graphite C<sub>1-6</sub> was obtained by the doping treatment as described in Example 3 with use of nitric acid as dopant. Synthetic resin paint A<sub>13</sub> (50 wt. percent) was introduced into a three-roll calender as in Example 2. To the resulting product were gradually added 25 wt. percent of carbon black (B<sub>2</sub>) and 25 wt. percent of doped graphite (C<sub>1-6</sub>). The resulting mixture was kneaded to an electrically conductive paint and the properties of the latter were measured.



The results are shown in Table 3.

#### Example 5

Powders of graphite  $C_1$  were introduced in a stainless steel vessel, from which the air was evacuated. Arsenic fluoride (V) was introduced into the vessel to a pressure of 250mm Hg. Doping was carried out at this pressure for 5 days. 30 wt. percent of polypropylene ( $A_9$ ) and 5 wt. percent of carbon black ( $B_2$ ) were introduced into the pressure kneader of the Example 3 and kneaded for 10 minutes. To the resulting kneaded product were added 65 wt. percent of the doped graphite  $C_1 - 7$ . The resulting mixture was kneaded for two minutes and prepared into a sheet, 1mm thick the properties of which were then measured. The results are also shown in Table 3.

Table 3 Properties of the Ultimate  
Plastic-Complex Materials

	<u>Sample Form</u>	<u>Electric Conductivity</u> $\text{ohm}^{-1} \text{ cm}^{-1}$	<u>Tensile Strength</u> $\text{kg/mm}^2$
Ex. 1-(1)	sheet	5	390
1-(2)	"	6.5	450
1-(3)	"	4	400
1-(4)	"	6.5	460
Ex. 2	liquid	10	2.3 poise (30°C)
Comp. Ex. 1-1	sheet	$10^{-17}$	370
1-2	sheet	$5 \times 10^{-3}$	380
2	liquid	$10^{-17}$	1.5 poise (30°C)
Ex. 3-(1)	sheet	$5 \times 10^2$	360
3-(2)	sheet	$2 \times 10^2$	310
3-(3)	sheet	$9 \times 10^2$	350
3-(4)	sheet	$7 \times 10^2$	350
3-(5)	sheet	$5 \times 10^2$	330
4	liquid	$8 \times 10^3$	3.6 poise (30°C)
5	sheet	$2 \times 10^3$	290

It is seen from the results shown in the above Table that the inventive material is significantly improved in electrical conductivity over the conventional material and compared favorably therewith in mechanical behavior, owing to the use of graphite and carbon black simultaneously, although the amount of additives to the synthetic resin material is same as used in the conventional electrically conductive material.

#### Example 6

The materials of the compositions shown in Table 4 below were kneaded together in a Banbury mixer and pelletized in a pelletizer. The resulting products were pressed by a heating press into 100 x 100 mm sheets each 1mm thick. The pressing conditions were 200°C temperature and 300 kg/cm<sup>2</sup> pressure.

The compositions (in wt. percents) for the present and Comparative Example are shown in Table 4.

Table 4 Compositions (wt. % )

Mat. Test No.	synth. resin mat. (A)	elec. cond. carb. black (B)	inorg. filler (C)	dens. of synth. resin mat. (g/cm <sup>3</sup> )
6-(A)	A <sub>4</sub> 45.5	B <sub>4</sub> 54.5	-	0.950
b-(2)	A <sub>5</sub> 95.2	B <sub>2</sub> 4.8	-	0.961
6-(3)	A <sub>6</sub> 40.0	B <sub>5</sub> 20	C <sub>2-2</sub> 40	0.957
6-(4)	A <sub>3</sub> 24.7	B <sub>3</sub> 1.2	C <sub>3</sub> 74.1	0.958
6-(5)	A <sub>3</sub> 48.8	B <sub>2</sub> 2.4	C <sub>4</sub> 48.8	"
6-(6)	A <sub>4</sub> 50.0	B <sub>4</sub> 25.0	C <sub>5</sub> 25.0	0.950
6-(7)	A <sub>6</sub> 18.2	B <sub>3</sub> 9.1	C <sub>4</sub> 72.7	0.957
Comp. 3-1	A <sub>4</sub> 43.5	B <sub>4</sub> 56.5	-	0.950
3-2	A <sub>7</sub> 95.2	B <sub>2</sub> 4.8	-	0.935

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Test results for the sheet are shown in Table 5.

Table 5 Test results

properties Test. No.	vol. resis. (ohm cm)	tens. str. ret. ratio (%)
6-(1)	0.8	87
6-(2)	$2 \times 10^2$	98
6-(3)	2.2	97
6-(4)	$3 \times 10^2$	97
6-(5)	$3 \times 10^2$	96
6-(6)	3.8	85
6-(7)	2.5	96
Comp. 3-1	test piece not made	test piece not made
3-2	$1.8 \times 10^2$	40

It is seen from the test results shown in Table 5 that the sheet manufactured from a mixture of polyethylene with density higher than 0.94 and at least one additive selected from the group consisting of calcium carbonate, talcum, alumina, silica and titania has an improved tensile strength retention ratio over the sheet manufactured from a mixture of polyethylene with density not higher than 0.94 and not containing these additives (calcium carbonate).

It is seen from the comparative Example 3-1 that the plastic complex material becomes difficult to form a sheet when more than 120 wt. parts of carbon black are added to 100 wt. parts of polyethylene.

#### Example 7

The materials of the compositions shown in Table 6 below were injected into a pressure kneader heated to 180°C, kneaded for 15 minutes and pressed into sheets each 1mm thick by a calender unit.

Table 6 Compositions (wt. %)

Start. Mat. Test No.	Synth. resin mat. (A)	elec. cond. carbon black(B)	inorg. filler talc (C <sub>2</sub> )
Ex. 6-(1)	A <sub>12</sub> : 62.5	B <sub>4</sub> : 31.3	C <sub>2-1</sub> : 6.2
Comp. Ex. 3-1	" : 66.7	" : 33.3	-
Ex. 6-(2)	A <sub>2</sub> : 34.5	B <sub>3</sub> : 17.2	C <sub>2-2</sub> : 48.3
Com. Ex. 3-2	" : 66.7	" : 33.3	-
Ex. 6-(3)	A <sub>1</sub> : 46.4	B <sub>1</sub> : 33.3	C <sub>2-1</sub> : 19.1
Comp. Ex. 3-3	" : 58.8	" : 41.0	-
Ex. 6-(4)	A <sub>9</sub> : 47.6	B <sub>3</sub> : 42.9	C <sub>2-2</sub> : 9.5
Comp. Ex. 3-4	" : 52.6	" : 47.4	-

Then, the volume resistivity of the resulting samples was measured as a function of temperatures. The results are shown in Fig. 2.

In this figure, curves a-1-4 and b-1-4 stand for values obtained with Examples 7-1-4 and comparative Examples 4-1-4, respectively.

It is seen from this figure that the samples a-1-4 with talcum contents are subject to only minor changes in volume resistivity relative to variation of temperature as compared to the samples b-1-4 without talcum contents, and that the volume resistivity itself of the samples a-1-4 is lowered.

#### Example 8

High-density polyethylene was used as base synthetic resin material to which were added carbon black and graphite to provide a basic composition to which was added pulverulent active carbon to provide the composition shown in Table 7. This electrode composition was kneaded thoroughly in a pressure kneader at an initial temperature of  $180^{\circ}\text{C}$  and for 3 minutes at 60 rpm, and then kneaded for 12 minutes at 90 rpm. The kneaded material was clamped between heat press mold halves, pre-heated at  $150$  to  $170^{\circ}\text{C}$  for 5 minutes, then pressed for 5 minutes at  $100\text{ kg/cm}^2$  to an electrode sheet 1mm thick.

Table 7 Electrode Composition

Test No.	Electrode Composition (wt. %)				
	basic composition			active carbon	kind of active carbon
	*1 synthetic resin material $A_8$	*2 composition carbon black $B_2$	*3 graphite $C_1$		
Ex. 8-(1)	50	20	20	10	powdered active carbon Shirasagi A (manuf. by Takeda Yakuhiin Kogyo K.K.)
Ex. 8-(1)	50	20	20	10	powdered active carbon Shirasagi M. (manuf. by Takeda Yakuhiin Kogyo K.K.)
Ex. 8-(3)	50	20	20	10	powdered active carbon Carbo-Raffin (manuf. by Takeda Yakuhiin Kogyo K.K.)
Comp. Ex. 5-1	50	20	30	-	

\* 1 Polyethylene; density  $0.963 \text{ g/cm}^2$ , melting point  $132^\circ\text{C}$ ; MFR  $5.3 \text{ g/10min}$ .

\* 2 Carbon black; Ketchen Black EC (Lion Acso)

\* 3 Graphite; G-200 under (Tokai Carbon)



The electrode thus obtained may be used in a bromine-zinc battery as typical of the secondary battery and diffusion of bromine as its active material was measured with the test piece of electrode by the device shown in Fig. 3 in the manner described above. The results are shown in Fig. 4.

It is seen from this figure that bromine diffusion differed markedly depending on whether active carbon has been added or not and that bromine diffusion is lowest with Shirasagi A No. 8-(1), and proceeds through a medium value with Shirasagi M No. 8-(2) to a maximum value with Carbo-Raffin No. 8-(3).

Next, electrode test samples No. 8-(1) - (3) and No. 5-1 were immersed in 95% bromine solution for 500 hours at room temperature and changes caused in tensile strength and volume resistivity were measured. The results are shown in Table 8 below.

Table 8 Electrode Characteristics

Test No.	Tensile Strength (kg/cm <sup>2</sup> )		reduction rate (%)	volume resistivity (Ωcm)		
	initial	after 500 hrs		initial	after 500 hrs	increase rate (%)
Ex. 8-(1)	375	363	3.2	0.105	0.109	3.8
Ex. 8-(2)	373	361	3.1	0.106	0.110	3.8
Ex. 8-(3)	375	361	4.0	0.105	0.111	5.7
Comp. Ex. 5-1	300	257	14.3	0.174	0.200	14.9

CLAIMS:

1. An electrically conductive plastic complex material comprising a synthetic base resin material, electrically conductive carbon black, and an inorganic filler, characterized in that the inorganic filler comprises at least one of graphite, calcium carbonate, talcum, alumina, silica and titania.
2. A material according to Claim 1 characterized in that it comprises 30 to 80 wt. % of the synthetic base resin material, 5 to 40 wt. % of electrically conductive carbon black and 5 to 65 wt. percent of graphite as inorganic filler.
3. A material according to Claim 2 characterized in that the graphite is pre-treated with at least one dopant.
4. A material according to Claim 3 characterized in that the dopant comprises at least one of bromine, iodine, iodine chloride, iodine bromide, sulfuric acid, nitric acid and arsenic fluoride (V).
5. A material according to any of Claims 1 to 4 characterized in that the synthetic base resin material is an olefinic polymer such as polypropylene, polyethylene or ethylene-propylene copolymer or polyester resin paint.
6. A material according to Claim 1 characterized in that the synthetic base resin material is an olefin polymer, and the inorganic filler is graphite, the mixture additionally containing adsorptive active carbon and being formed to a predetermined shape.
7. A material according to Claim 6 characterized in that the material is formed and used as halogen battery electrode.

FIG. 1

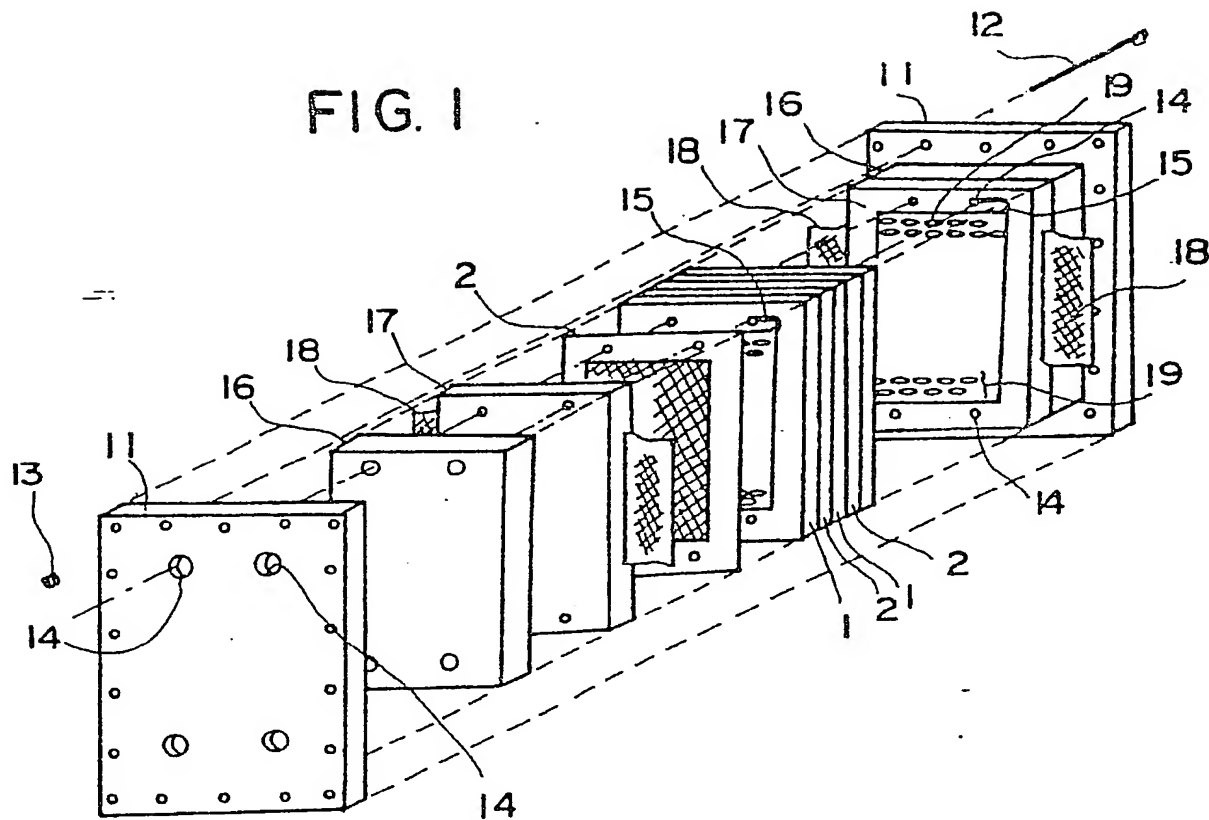
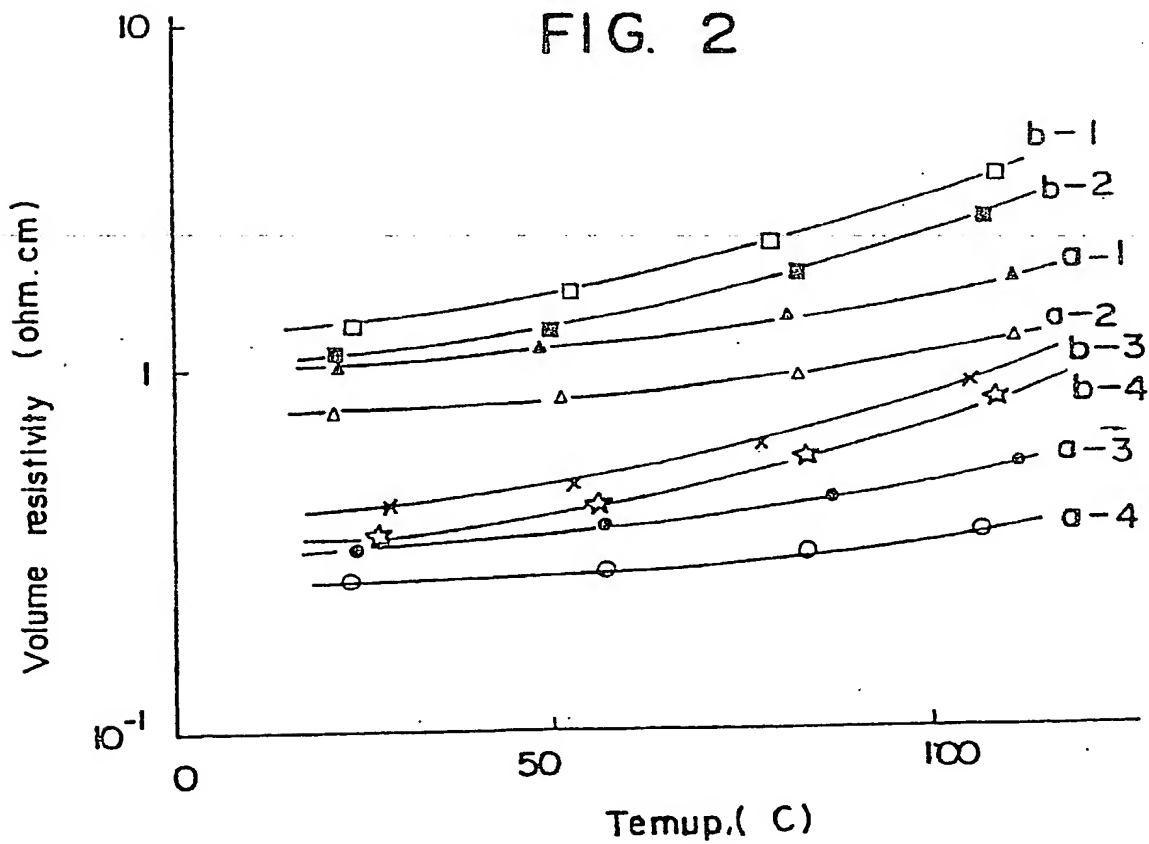
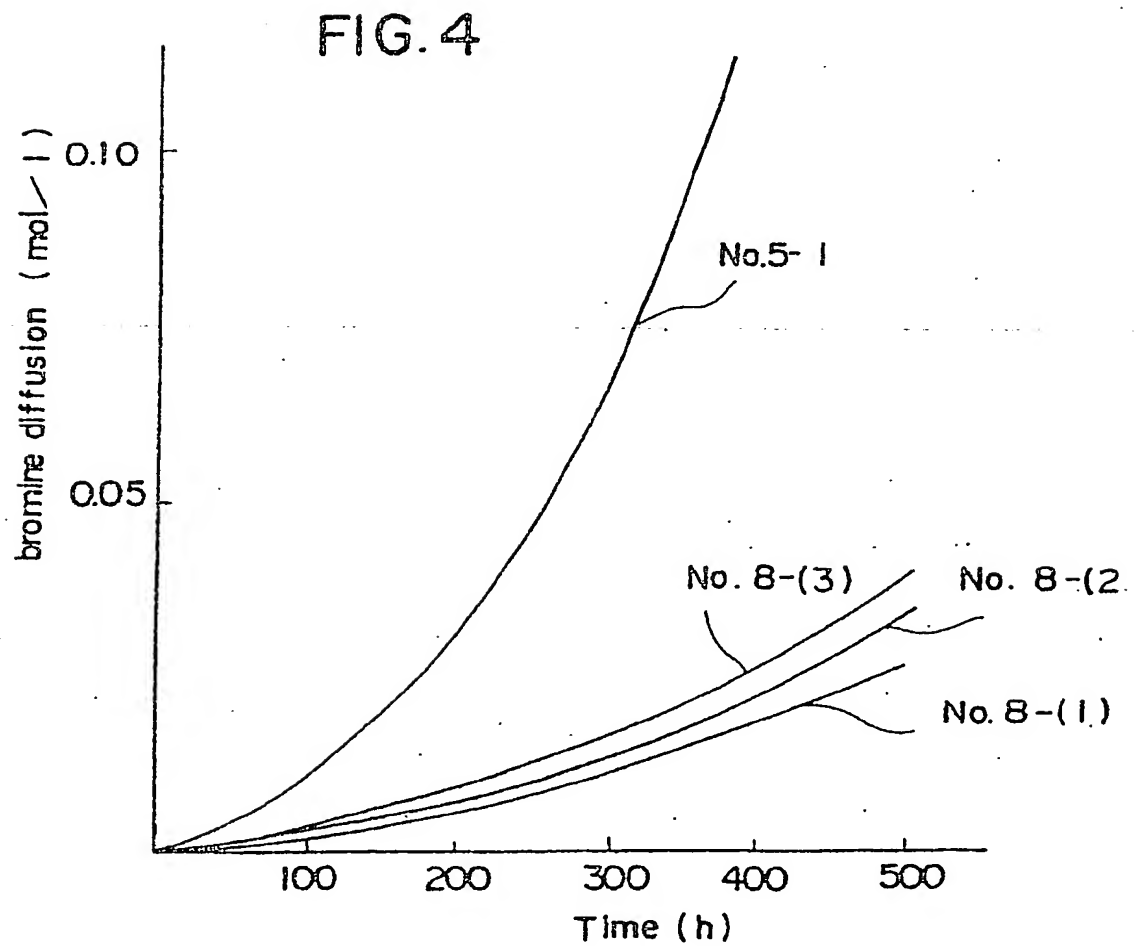
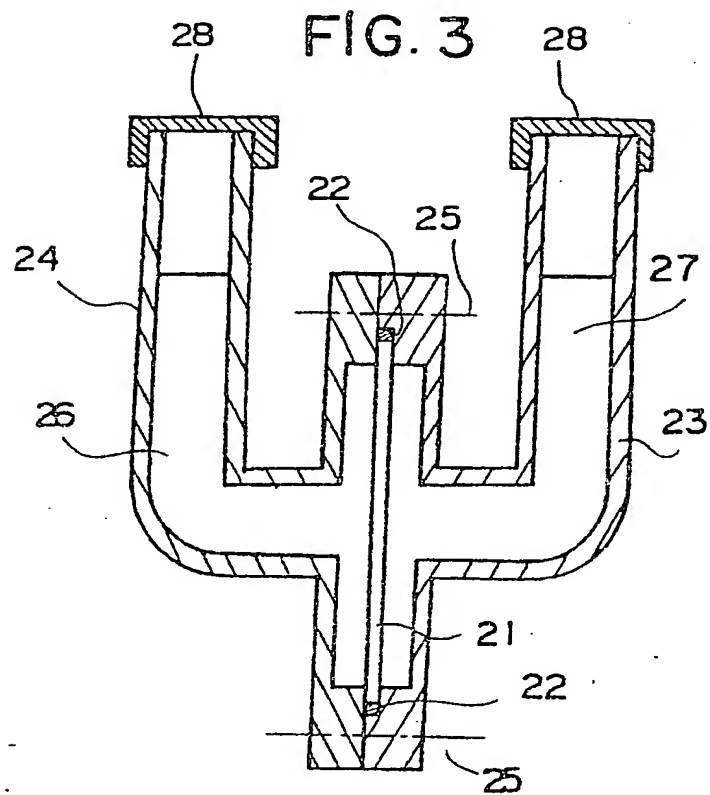


FIG. 2







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# EUROPEAN SEARCH REPORT

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Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 83306986.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	DE - A1 - 2 923 245 (GUTEHOFFNUNGS-HÜTTE)  * Claim 1 *	1,2,5	H 01 B 1/24 H 01 M 4/66 C 09 C 1/46 C 08 K 3/04
X	CH - A - 554 589 (RHONE-POULENC)  * Claim 1; column 1, lines 20-22; column 2, lines 12-17; column 4, example 5 *	1,2,5-8	
Y		3,4	
Y	JP - A2 - 57-177 066 (DAIKIN KOGYO)  * Claims 1-3 *	3,4	
P	& PATENT ABSTRACTS OF JAPAN, unexamined applications, C-field, vol. 7, no. 19, January 25, 1983  THE PATENT OFFICE JAPANESE GOVERNMENT (C-147)(1164), page 148 C 147  * Kokai-no. 57-177 066 (DAIKIN KOGYO) *		TECHNICAL FIELDS SEARCHED (Int. Cl. 7)  H 01 B H 01 M C 09 C 1/00 C 08 K 3/00 C 08 L
X	DE - A1 - 2 524 640 (EXXON)  * Claims 1,4,5,10; page 7, last paragraph *	1,5-8, 11	
X	DE - A1 - 2 834 390 (PREH)  * Claims 1,4; page 8, lines 17-21; page 13, example 1 *	1,9	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 03-02-1984	Examiner KUTZELNIGG
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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EP 83306986.7

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>EP - A2 - O 038 713 (RAYCHEM)</u> * Claims 1,2; page 5, lines 4-5 * ---	1	
A	<u>EP - A1 - O 038 718 (RAYCHEM)</u> * Abstract; page 10, lines 11-12 * ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.)